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Determination of Thermal Constants and Other Molecular Properties of Strong Acids by Differential Temperature Model (DTM)

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Abstract
Ionization potentials of strong acids in solution have been studied following oxonium formation route using Differential Temperature Model (DTM). The study has led to the discovery of a new chemical hypothesis which provides mathematical model for the determination of thermal constants and other molecular properties of strong acids in solution.

Keywords: Thermal constants; Strong acids; Differential temperature

1.0 Introduction

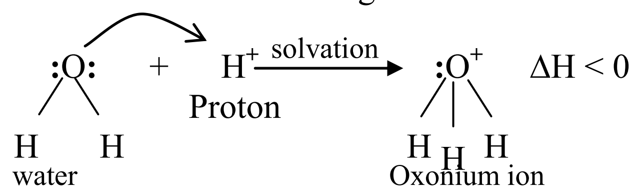
Strong acids are strong electrolytes with high ionization potentials in solution, yielding complete cations and anions without reserved acid molecules in equilibrium with the ions.

$$H - A_{(g)} + aq \rightarrow H^{+}_{(aq)} + A^{-}_{(aq)} \qquad \Delta H > 0 \qquad \ldots \quad 1$$

The ionisation process is an endothermic process. A lattice energy is absorbed by the reacting system and thus, is responsible for the breaking of the bonds between elements.

According to the proton theory of acids, developed by Bronsted and Bjerrum in Denmark and Lowry in England in 1923[1]. The discharged proton (H^+), has a great tendency to be solvated, being an empty orbital. It then implies that, a proton does not exist in a free state in solution but"married" to water molecule by solvation producing the so called oxonium ion in solution.

The formation of oxonium is an exothermic process whereby hydration or solvation energy in the form of heat is being evolved[2-3].



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The extent to which an acid ionises or dissociate in solution depends upon the intrinsic acidic strength and upon the degree of affinity of the solvent for proton (protophilicity). Water is therefore a good solvent for ionisation of strong acids because it is highly protophilic.

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1.1 Experimental

Five strong acids namely H_2SO_4, HNO_3, HCl, HBF_4 and H_3PO_4 were purchased from BDH Chemical Limited and used as purchased. The solvent was bi-distilled water.
The reaction (dissolution of each acid) was carried out in a well- insulated vessel, known as calorimeter.
Since it was insulated, it could effectively measure the heat energy transferred during the reaction[4]. Dewar flask was used as calorimeter as shown in Fig 1.

The flask was suited for the measurement due to its large heat capacity. The inner surface of the flask was silvered and a space between the inner and outer walls was evacuated in order to minimize exchange of heat energy with the surroundings.

A cork stopper was fitted at the top of the mouth and it contained a thermometer. The differential temperature was measured by thermometry.

The heat evolved from each solution was measured in calories and converted to Joules. The gram-calories is the amount of heat required to raise the temperature of 1g of water through 1°C. the amount of heat evolved in each process was measured as mass of the system multiplied by differential temperature and multiplied by specific heat of the system.

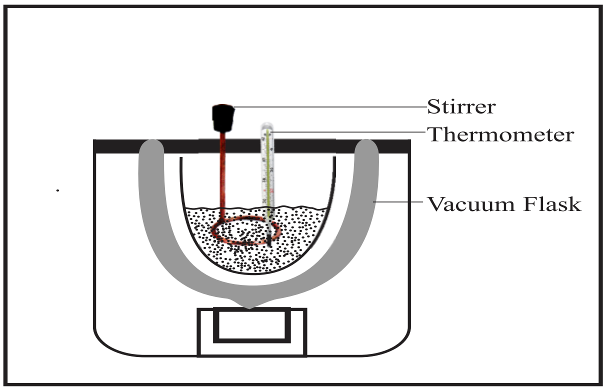

Fig. 1: **Dewar Flask for Thermochemical Measurements**

1.2 The New Propounded Chemical Hypothesis

Continuous research and measurement of the variation between the thermal potentials and molecular properties of the ionised species in solution have led to the discovery of a new chemical hypothesis as propounded below.

"At constant temperature and pressure, the change in temperature ΔT of the dilution of equal volumes of strong acids in a fixed volume of water is directly proportional to the product of the sum of the relative masses of the ionised species and the square of the basicity of the acid"

1.3 Mathematical Implication of the Hypothesis

$$\Delta T \propto b^2(M_{C^+} + M_{a^-}) \quad \ldots \quad \ldots \quad 3$$

Where M_{C^+} and M_{a^-} are the relative masses of the cation and anion species respectively and b, the basicity of the acid. ΔT is the change in temperature between the maximum temperature attained after dilution and the initial temperature of the solvent (water) before dilution.
If a constant is introduced into the proportion in 1 above, we obtain

$$\Delta T = kb^2(M_{C^+} + M_{a^-}) \quad \ldots \quad \ldots \quad 4$$

Where k is the thermal constant of strong acids at equivalent dilution at constant temperature and pressure.

From Eqn. 2, $k = \frac{\Delta T}{b^2(M_{c^+} + M_{a^-})}$ … … 5

1.4 Determination of Thermal Constant k

The calculation of thermal constant k published elsewhere[5] is hereby represented for

HCl and H_2SO_4. The same procedures apply for other strong acids taking cognizance of the number of protons discharged (basicity).

1.4.1 HCl

The ionization and subsequent formation of oxonium for HCl in solution follows the mechanism.

$$H_2O_{(l)} + HCl_{(l)} \rightarrow H^+_{(aq)} + Cl_{(aq)} \xrightarrow{H_2O} H_3O^+_{(aq)} + Cl^-_{(aq)} \quad \Delta H < O \ldots \quad 6$$

$$M_{C^+} = M_{H_3O^+} = 19; \quad M_a^- = M_{Cl}^- = 35.5$$

$$(M_c^+ + M_a^-) = (19 + 35.5) = 54.5$$

$$\text{For HCl, } k = \frac{\Delta T}{b^2(M_{c^+} + M_{a^-})} = \frac{\Delta T}{54.5} \quad \ldots \quad \ldots \quad 7$$

1.4.2 H_2SO_4

The ionization and subsequent formation of oxonium for H_2SO_4 in solution follows the mechanism.

$$H_2O_{(l)} + H_2SO_{4(l)} \rightarrow 2H^+_{(aq)} + SO_4^{2-}{}_{(aq)} \xrightarrow{H_2O} 2H_3O^+_{(aq)} + SO_4^{2-}{}_{(aq)} \quad \Delta H < O \ldots \quad 8$$

$$M_{c^+} = 2M_{H_3O} = 38; \quad M_a^- = M_{SO_4^{2-}} = 96$$

$$(M_c^+ + M_a^-) = (38 + 96) = 134$$

$$\text{For } H_2SO_4, k = \frac{\Delta T}{b^2(M_{c^+} + M_{a^-})} = \frac{\Delta T}{536} \quad \ldots \quad \ldots \quad 9$$

1.5 Results and Discussion

1.5.1 Results

The results obtained from the measurement for the various acids are presented in Tables 1 to 5.

Table 1(a): Thermal constants for HCl at various dilutions

Percentage Dilution (v/v%)	T_1 (K)	T_2 (K)	ΔT (K)	k (Kmol g^{-1})	b
15	303	309	6.00	0.11	1
20	303	311	8.00	0.15	1
25	303	312.5	9.50	0.17	1
30	303	315	12.00	0.22	1
35	303	316	13.00	0.24	1

Table 1(b): Values of basis constant, Hydrobasic constants and Thermohydrobasic constants of HCl at various dilutions

Percentage Dilution (v/v%)	Basic constant kb^2 (mole)	Hydrobasic constant $18kb^2$ (g)	Thermohydrobasic constant $\Delta T\text{-}18kb^3$ (g)
15	0.11	1.98	4.02
20	0.15	2.70	5.30
25	0.17	3.06	6.44
30	0.22	3.96	8.04
35	0.24	4.32	8.68

Table 2(a): Thermal constants for HNO_3 at various dilutions

Percentage Dilution (v/v%)	T_1 (K)	T_2 (K)	ΔT (K)	k (Kmol g^{-1})	b
15	303	313	10.0	0.12	1
20	303	316	13.0	0.16	1
25	303	318	15.0	0.18	1
30	303	320	17.0	0.21	1
35	303	322	19.0	0.24	1

Table 2(b): Values of basis constant, Hydrobasic constants and Thermohydrobasic constants of HNO_3 at various dilutions

Percentage Dilution (v/v%)	Basic constant kb^2 (mole)	Hydrobasic constant $18kb^2$ (g)	Thermohydrobasic constant $\Delta T\text{-}18kb^3$ (g)
15	0.123	2.214	7.786
20	0.160	2.880	10.120
25	0.185	3.330	11.670
30	0.210	3.780	13.220
35	0.235	4.230	14.770

Table 3(a): Thermal constants for H_2SO_4 at various dilutions

Percentage Dilution (v/v %)	T_1 (K)	T_2 (K)	ΔT (K)	k (Kmolg^{-1})	b
15	303	313	10	0.010	2
20	303	316	13	0.024	2
25	303	318	15	0.028	2
30	303	320	17	0.032	2
35	303	322	19	0.035	2
40	303	324	21	0.039	2

Table 3(b): Values of basis constant, Hydrobasic constants and Thermohydrobasic constants of H_2SO_4 at various dilutions

Percentage Dilution (v/v%)	Basic constant kb^2 (mole)	Hydrobasic constant $18kb^2$ (g)	Thermohydrobasic constant $\Delta T\text{-}18kb^3$ (g)
15	0.040	0.720	8.560
20	0.096	1.728	9.544
25	0.112	2.016	10.968
30	0.128	2.304	12.392
35	0.140	2.520	13.960
40	0.156	2.808	15.384

Table 4(a): Thermal constants for HBF_4 at various dilutions

Percentage Dilution (v/v %)	T_1 (K)	T_2 (K)	ΔT (K)	k ($Kmolg^{-1}$)	b
10	298	299	1.0	0.009452	1
20	298	300	2.0	0.018904	1
30	298	301	3.0	0.028355	1
40	298	301	3.0	0.028355	1
50	298	302	4.0	0.037807	1
60	298	303	5.0	0.047170	1

Table 4(b): Values of basis constant, Hydrobasic constants and Thermohydrobasic constants of HBF_4 at various dilutions

Percentage Dilution (v/v%)	Basic constant kb^2 (mole)	Hydrobasic constant $18kb^2$ (g)	Thermohydrobasic constant $\Delta T\text{-}18kb^3$ (g)
10	0.009452	0.170	0.830
20	0.018904	0.340	1.660
30	0.028355	0.510	2.490
40	0.028355	0.510	2.490
50	0.037807	0.681	3.319
60	0.047170	0.849	4.151

Table 5(a): Thermal constants for H_3PO_4 at various dilutions

Percentage Dilution (v/v%)	T_1 (K)	T_2 (K)	ΔT (K)	k ($Kmolg^{-1}$)	b
10	301	305	4.0	0.002924	3
20	301	309	8.0	0.005848	3
30	301	313	12.0	0.008772	3
40	301	318	17.0	0.012427	3
50	301	319	18.0	0.013158	3
60	301	320	19.0	0.013889	3

Table 5(b): **Values of basis constant, Hydrobasic constants and Thermohydrobasic constants of H_3PO_4 at various dilutions**

Percentage Dilution (v/v%)	Basic constant kb^2 (mole)	Hydrobasic constant $18kb^2$ (g)	Thermohydrobasic constant $\Delta T\text{-}18kb^3$ (g)
10	0.02632	0.47376	2.5789
20	0.05263	0.94734	5.1579
30	0.07895	1.42110	7.7368
40	0.1118	0.20124	10.9605
50	0.1184	0.21315	11.2505
60	0.12500	2.25000	12.2499

1.5.2 Discussion

The S.1 units of the various constants as deducted from the experimental measurements are summarized in Table 6.

Table 6: S.I. Units of some parameters

Name of Constant	S.I. Unit
Thermal constant k	$Kmolg^{-1}$ Kelvin mole per gramme
Basic constant kb^2	Mole
Hydrobasic constant $18kb^2$	(g) gramme
Thermohydrobasic constant $\Delta T\text{-}18kb^3$	(g) gramme

Thermal constant measures the amount of temperature and moles of ionized species expended per gramme of solution.

Basic constant measure the total number of moles of ionized acid expended in solution.

Hydrobasic constant measures the amount in grammes of the aqueous acid expended in the ionization process.

Hydrobasic constant measures the amount in grammes of the acqueous acid expended in the ionisation process.

Thermohydrobasic constant measures the amount in grammes of the ionized acid expended in solution during the process of ionization.

1.5.3 Relationship between Basic Constant and Thermohydrobasic Constant

Table 1-5 reveals a direct proportional relationship between kb^2 and $\Delta T\text{-}18kb^3$. In each case, a plot of kb^2 (mole) versus $\Delta T\text{-}18kb^3$ (g) for the experimental acid produces a straight line which slope is the reciprocals of the molecular mass of the acid.

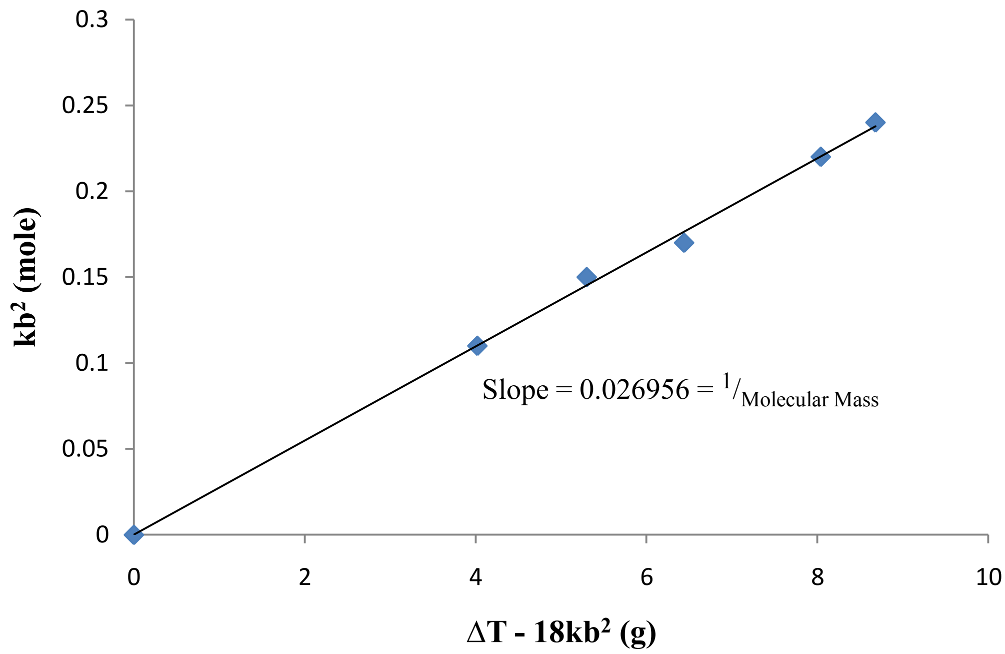

Fig. 2: Plot of basic constant (mole) versus thermohydrobasic constant (g) for the determination of molecular mass of HCl

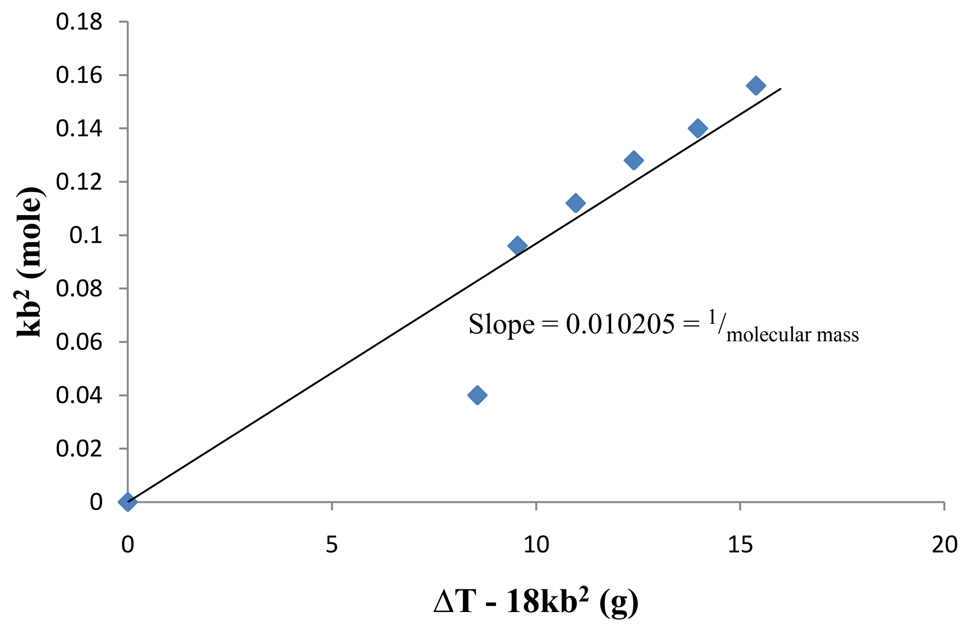

Fig. 3: Plot of basic constant (mole) versus thermohydrobasic constant (g) for the determination of molecular mass of H_2SO_4

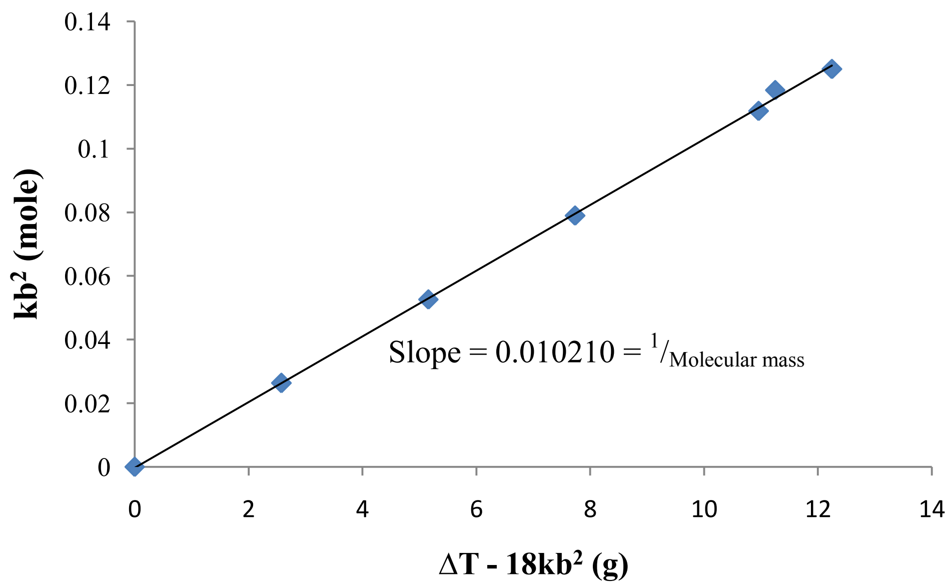

Fig. 4: Plot of basic constant (mole) versus thermohydrobasic constant (g) for the determination of molecular mass of H_3PO_4

The various slopes obtained for the various plots are summarized in Table 7. The reciprocal of the slopes give the exact molecular mass of the acid undergoing ionization.

Table 7: **Experimental and actual molecular masses of the acids**

Acid	Slope	Experiment Molecular mass	Actual molecular mass
HCl	0.026956	37 $gmol^{-1}$	36.50
HNO_3	0.015712	63.4 $gmol^{-1}$	63.00
H_2SO_4	0.010205	97.9 $gmol^{-1}$	98.00
HBF_4	0.011391	87.79 $gmol^{-1}$	87.81
H_3PO_4	0.010210	97.94 $gmol^{-1}$	97.99

1.5.4 **Relationship between ΔT and k**

A plot of ΔT versus k(M_{c^+} + M_{a^-}) at various dilutions produces a straight line with slope equal to the square of the number of ionized proton (basicity) of the acid.[6] Subsequently, the square root of the slope gives the exact number of moles of ionized proton in solution. This plot is demonstrated below for H_3PO_4 in Fig. 5.

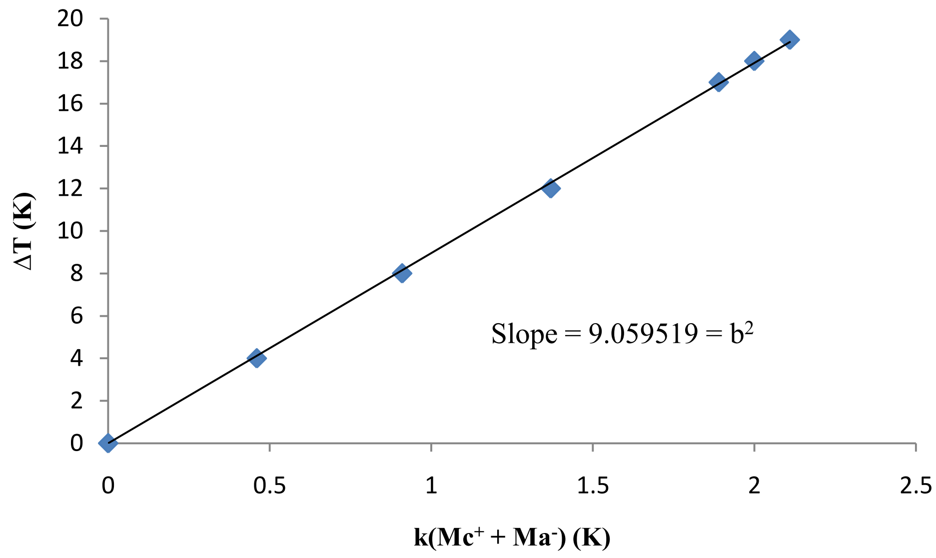

Fig. 5: Plot of Differential Temperature (ΔT) versus k(M_{c^+} + M_{a^-})for the determination of ionizable protons in H_3PO_4

1.5.5 **Oxonium Law (Hypothesis)**

The result of the Hypothesis has given birth to Oxonium hypothesis (Law) stated as follows:

> **"At constant temperature and pressure, the thermal constants of all strong acids are equal at equivalent dilutions"**.

Thus; $k_1 = k_2 = k_3$ = a constant … … 10

Where 1, 2, 3 …. represent different strong acids. The expanded form of

Eqn. 10 is $\frac{\Delta T_1}{b^2(M_{c^+} + M_{a^-})} = \frac{\Delta T_2}{b^2(M_{c^+} + M_{a^-})}$ … … 11

1.5.6 **Application of the Present Study to Chemical Studies**

The present research and discovery has added new chapter for numerous chemical calculations of molecular properties of strong acids such as calculation of molecular mass by Differential Thermal method (DTM) calculation of thermal constants, basic constant, hydrobasic constant and thermohydrobasic constant.

Sample questions are provided below.

1. Determine the Thermal constant for HCl if the differential temperature is 20°C.
2. The initial temperature of solvent is 25°C. Determine the final temperature of H_2SO_4 in solution if the thermohydrobasic constant is 21.2g.
3. The basic constant of H_2SO_4 is 0.32 mole. Calculate the number of moles of protons discharged by H_2SO_4 at the differential temperature of 45K.

4. At T_2 = 350.3K, the Hydrobasic constant of H_2SO_4 is 12.96g. Determine T_1

5. The initial temperature of solvent for the dissolution of H_2SO_4 is 300k. Determine the maximum temperature of ionization, if the differential temperature of HCl at the same dilution is 3.3K. Hence prove that the formation of oxonium has taken place in the ionized solution.

1.5.7 Recommendations

The author believe that the Oxonium Hypothesis and the Differential Temperature Model (DTM) arising from the discoveries of this research will generate chemical interests among the various national and international chemical societies such that the new chemical hypothesis would be adopted and upgraded to theory or law for their application and further advancement of chemical studies.

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